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Photoelectrochemistry

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On the Way to Artificial Photosynthesis: Simple Materials and System Designs for Photoelectrodes

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Natural photosynthesis converts solar energy, water, and carbon dioxide into energy-rich carbohydrates and releases oxygen; this process sustains all forms of life on Earth and powers all human activities, directly or indirectly. This has long motivated extensive research activity in chemistry, biology, physics, and materials science to understand and even to mimic such biological energy-transfer processes using artificial materials and technologies to achieve water splitting, CO_2 fixation, green organosynthesis, and environmental purification through sunlight.

A crude search of digital data bases gave about 125000 publication items during the past 20 years on the subject. Since Japanese scientists first took on the challenge using titanium dioxide to split water in 1972,[1] a variety of molecular and solid-state substances have been examined as photocatalysts for solar energy conversion. However, after 40 years of investigation, the core problem is still related to the lack of solar energy transducers ("antennae"), which are required to be efficient, stable, abundant, and especially capable of working with light of the visible spectrum or even longer wavelengths. Several recent reviews have discussed more than 120 materials previously developed, but mainly focused on UV-active semiconductors and modified TiO_2 materials.

There is increased activity in this mature but still developing area because of current efforts to address global energy and environmental problems in a sustainable manner. Indeed, many governments have launched big joint research centers and teams (like "The Joint Center for Artificial Photosynthesis" in Cal Tech and Berkeley, and the "Light2-Hydrogen" project in Germany) in an effort to achieve breakthrough innovations in energy production with artificial photosynthesis: the race has started up again.

In their current article[2] Allen J. Bard and his team describe a simple solid-state approach to generate boron arsenide powders from the elements by heating them in a quartz tube to 800 °C. The boron–arsenic system is rather complicated in terms of potential multiple stiochiometries; mixed compounds such as $B_{12}As_2$ and $B_{6-7}As$ easily form and are the preferred species at temperatures exceeding 1000 °C. The simplicity of the Bard approach towards the desired 1:1 stoichiometry, that is, making BAs, therefore is surprising. Indeed, additional experiments showed that a surface reaction takes place, converting the millimeter-sized boron particles into a rough, nanostructured surface layer of BAs (Figure 1) while a pure boron core remains. It is interesting that already the contrast of the SEM images (B black, BAs white) indicates the successful synthesis of semiconductor nanostructures with simple electron exit.

To generate a complete conduction pathway, these powders were partially coated with a thin gold layer by electrochemical deposition; this overall construction then served as the active antenna part of a photoelectrode. When this electrode was used in a photoelectrochemical cell, currents of around 0.1 $mA\,cm^{-2}$ and incident photo-to-electron conversion efficiencies (IPCEs) of 3 % (visible light) to 5 % (UV light) could be determined (Figure 2). When one considers the simplicity of the electrode synthesis, this is quite remarkable: no single-crystal growth, no semiconductor processes or cleanroom procedures—just convenient standard solid-state chemistry and electrochemistry techniques.

Why is this approach important? Photoelectrodes in photovoltaic cells are quite commonplace, with the efficiencies of commercial cells reaching 18 % on the device level, well above the reported values of the highlighted article. However the single-crystalline or polycrystalline silicon used in these cells is expensive to manufacture. The global consequence is that standard photovoltaic devices are is still not cost-effective, and without government subsidies this technology is not viable. Using photoelectrochemistry and cheap, *chemically* processed electrodes, one could not only make materials and devices significantly more cost-competitive, one simultaneously can make the step from in situ generated electrons, which are challenging to store and transport over extended times and distances (the net exergy in Europe is only 15 %), to chemical-storage molecules, created at the site of the generated electron and hole pairs. And we chemists certainly know that chemical molecules can be stored and transported in a more simple fashion. In short: it is an expressed opinion that photoelectrochemistry offer more advantages than photovoltaics, when price and logistics are considered.

I think it is fair to point out the potential weaknesses of the Bard system. At the moment, it still relies on methylviologen as an electron mediator, instead of really splitting water

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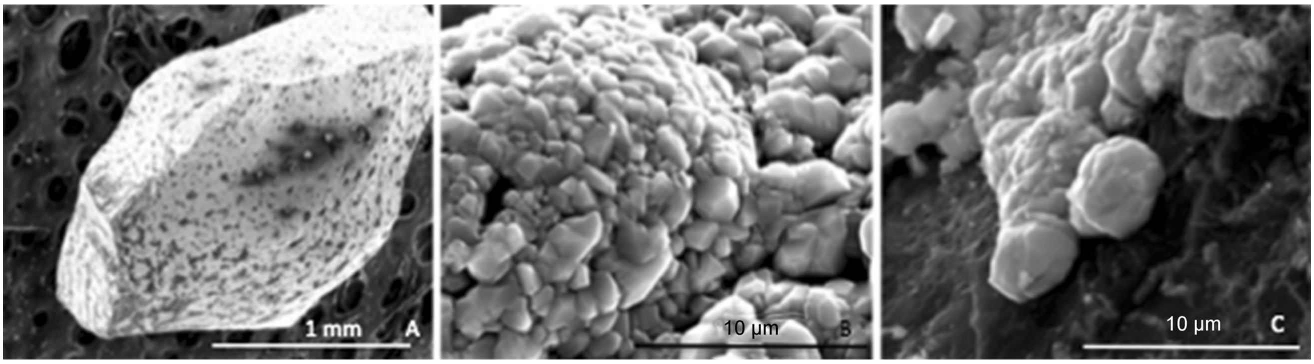

Figure 1. SEM images revealing the surface and core structure of the BAs-containing material prepared from granular boron. A) A single particle of BAs. B) Area of continuous BAs surface coverage. C) Area featuring a gap in the surface coverage. The light material is BAs and the dark material is the boron substrate. Taken from Ref. [2] with permission.

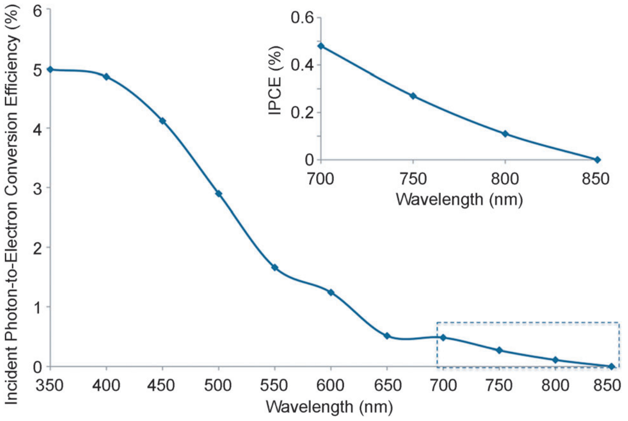

Figure 2. IPCE from a BAs crystal calculated from the net photocurrent at −0.25 V vs. Ag/AgCl in a 0.1 M aqueous Na_2SO_4 solution containing 0.01 M methylviologen. The inset shows the marked box on an expanded scale. Taken with permission from Ref. [2].

into the elements. For water splitting, the ideal cell voltage (calculated from the indirect band gap) of 1.46 V is presumably too small, and the overall band positions are presumably still not suitable, which also translates into a sensitivity against oxidation. Nevertheless, new developments in chemistry progress in many single steps, and all upcoming problems can be solved by further systematic work.

It is good for accelerating innovation in this area that there are competing materials on the market. Following the extensive work of Michael Grätzel et al. (e.g. Ref. [3]), the research group in Tokyo lead by K. Domen and K. Maeda[4,5] has published a rich oevre on inorganic solid-state semiconductors (metal oxynitrides and metal oxysulfides). These visible-light-sensitive materials can be tuned by variation of both the metal and the anion lattice to have both an appropriate band gap and band positions, and the full photochemical splitting of water was already shown. My personal favorite here is the work on GaN·ZnO.[6]

Our own work focusses on stable polymeric materials of the carbon nitride type, which are—most sustainable—available from the thermal condensation of, for example, urea.[7,8] This system has also already has shown its ability for the overall splitting of water, while the band gap can be modified by copolymerization schemes.[9]

I cannot predict which of the many systems will finally be the most successful, but it is an exciting thought that in this way chemistry can compete with physical approaches and contribute to solving some of our vital energy problems. Compared to the tremendous public support and funding of the diverse branches of photovoltaics, the research on photoelectrochemistry and photosynthesis is still rather innocent and academic. This is why there is certainly room for more research like Bard's work.

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